Toward Hexaphenylethane: Structure and Decomposition of Crystalline Triphenylmethyl Iodide

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Triphenylmethyl iodide ($C_{19}H_{15}I$) crystallizes in the monoclinic system: $a = 15.919(6)$ Å, $b = 10.826(6)$ Å, $c = 19.397(11)$ Å, $\beta = 114.86(4)°$, space group $C2/c$, $Z = 8$. In the structure, heterochiral propeller molecules are interdigitated. This arrangement, coupled with earlier reports of the thermal instability of triphenylmethyl iodide, suggested a convenient, topochemically controlled, solid-state synthesis of the elusive hydrocarbon hexaphenylethane. Crystals of the $^{13}C_{methyl}$-labeled triphenylmethyl iodide were heated to 100 °C in a rotor spinning at the magic angle within an NMR spectrometer. Spectral changes and accompanying analyses by plasma desorption mass spectrometry, calorimetry, and ESR spectroscopy reveal that the major product in the decomposition is triphenylmethane, produced by hydrogen atom abstractions from neighboring triphenylmethyl radicals, that subsequently oligomerize. These data provide a new view of the thermal stability of triphenylmethyl iodide in the solid state and an old view of the accessibility of hexaphenylethane.

Introduction

Triphenylmethyl iodide (**1**) was first described in Gomberg's 1900 paper[1] on the attempted synthesis of hexaphenylethane (**2**). Crystals of **1**, Gomberg remarked, turned dark "very readily" with the concomitant loss of iodine.[2] The isolation, he said, "requires considerable precautions as it is a very unstable body." Here, we report the crystal and molecular structure of **1**. Features of the crystallographic packing suggest that one consequence of the decomposition might be the formation of the still-elusive hydrocarbon **2**, in a restricted environment. If crystalline **1** does indeed decompose to give **2** it would mean that Gomberg did after all synthesize **2**, albeit by an unintentional route and unknowingly. We found this possible irony irresistible as we approach the centennial of Gomberg's first attempted synthesis of **2** and tested the possibility by following the decomposition of isotopically enriched **1** by solid-state NMR spectroscopy.

Crystal and Molecular Structure of Triphenylmethyl Iodide

We prepared **1** from triphenylmethanol and HI.[2] The yellow powder obtained in this way was recrystallized from CS_2 according to the original procedure of Gomberg.[1] The large golden crystals ({111}, {101}, {100}) indexed as monoclinic with $a = 15.919(6)$ Å, $b = 10.826(6)$ Å, $c = 19.397(11)$ Å, and $\beta = 114.86(4)°$ at 218 K; space group $C2/c$ with $Z = 8$.

The structure was solved by application of the Patterson function and subsequently refined. The intramolecular geometry of **1** is unremarkable (Figure 1). Comparable parameters are found in other molecularly isomorphous triphenylmethyl derivatives.[3] Atomic positional parameters are given in Table 1 (supporting information). The molecules sit on general positions related by a centers of inversion and forming pairs with C_i symmetry and approximate S_6 symmetry whereby heterochiral propellers are interdigitated pairwise and leaving iodine atoms to form close contacts with one another ($C_{methyl}-C_{methyl} = 5.76$ Å, $I-I = 5.14$ Å).[4] Figure 2 shows a space-filling model of three molecules of **1**, while Figure 3 shows a stereoview of the packed unit cell.

Proposed Synthesis of Hexaphenylethane

What happens when the supposed thermally unstable **1** decomposes in the solid state? It appeared to us that the molecules are well positioned to form the symmetrical dimer **2** following C−I bond scission and subsequent Walden inversion, as illustrated schematically in Figure 4. Reorientation of the radicals to form the solution dimer[5] might be slow under the constraints of the lattice. Organic solids often react under the influence of topochemical control to provide products that would not otherwise be obtained in fluid media.[6] Perhaps **2** would be accessible in the solid state through the topochemical decomposition of **1**.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Gomberg, M. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3150; *J. Am. Chem. Soc.* **1900**, *22*, 757.

(2) In 1965, **1** was described as follows: "Triphenylmethyl iodide is a troublesome compound; it darkens with liberation of iodine when exposed to light, forms the peroxide on contact with oxygen, undergoes homolysis to iodine and hexaphenylethane in non-polar solvents, reacts irreversibly with water to form carbinol, and is reduced to triphenylmethane by hydrogen iodide liberated in this hydrolysis." (Harmon, K. M.; Cummings, F. E. *J. Am. Chem. Soc.* **1965**, *87*, 539.) Exposure of **1** to moisture causes hydrolysis to triphenylmethanol and hydrogen iodide. **1** reacts with hydrogen iodide to form triphenylmethane and I_2, and hence blackening. This scheme is consistent with Gomberg's observation that the crystals of **1** are light sensitive. The reduction of **1** to triphenylmethane by hydrogen iodide is promoted by light because the homolysis of hydrogen iodide is light induced. When moisture was rigorously excluded from **1**, the crystals were not decomposed (i.e., changed color) by visible or ultraviolet light at 0 °C. Gomberg reported that his crystals were washed with petroleum ether and "dried rapidly *in vacuo*" and that the "crystals of the iodide can then be detached from the flask, and are at once put away in a closed bottle".[1]

(3) Triphenylmethyl chloride: Kahr, B.; Carter, R. L. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 79. Dunand, A.; Gerdil, R. *Acta Crystallogr., Sect. B* **1982**, *B38*, 570; Triphenylmethyl bromide: Dunand, A.; Gerdil, R. *Acta Crystallogr., Sect. B* **1984**, *B40*, 59. 1,1,1-Triphenylethane: Destro, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2495.

(4) This is a common packing motif for triphenylmethyl-X derivatives. See examples in ref 3.

(5) For a historical view of the triphenylmethyl equilibrium, see: McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

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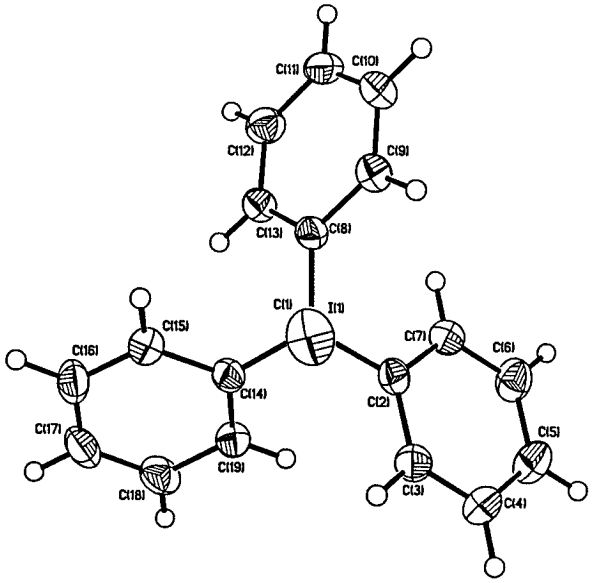


Figure 1. ORTEP representation of triphenylmethyl iodide (**1**) in the crystal viewed normal to the mean plane of the atoms.

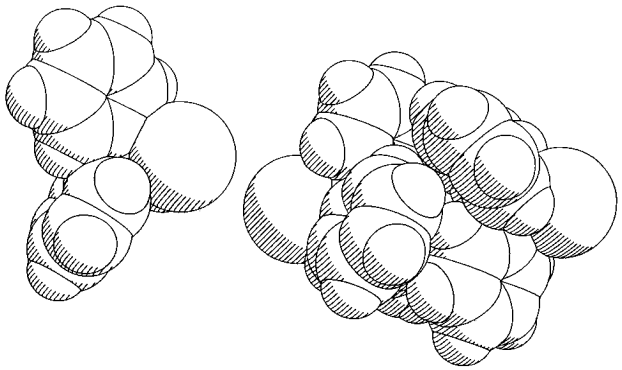


Figure 2. Space-filling representation of three of triphenylmethyl iodide (**1**) molecules in the crystal viewed perpendicular to the $C_{methyl}-C_{methyl}$ axis of the right most pair.

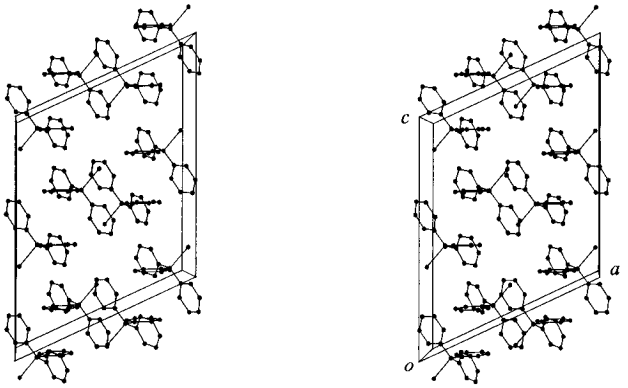


Figure 3. Stereoview of the unit cell packing of triphenylmethyl iodide (**1**) along the *b* axis.

It must be stressed that while the union of two carbon atoms separated by nearly 6 Å does not at first glance seem like a topochemically influenced transformation, the centers of mass of the phenyl rings remain nearly unchanged throughout the Walden inversion process. Focus on the actual spatial requirements of the dimer in Figure 2 rather than the schematic Figure 4.

Should this scheme conform to expectations, we would need a solid-state assay to confirm the presence of **2**.

(6) See, for example: Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

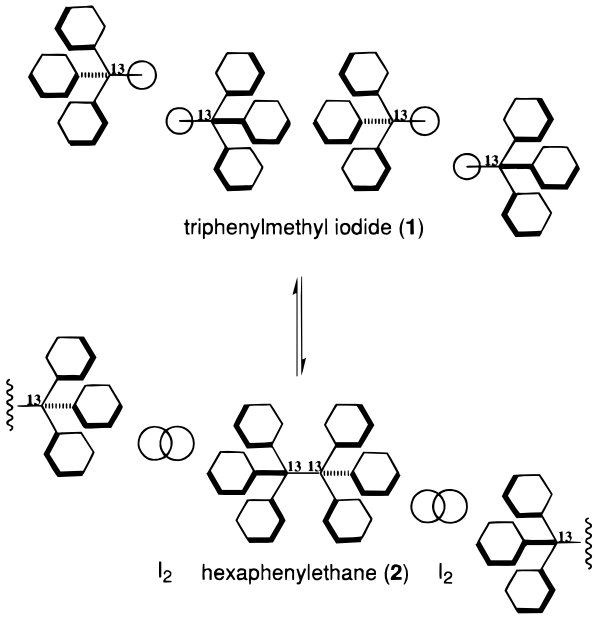


Figure 4. Schematic decomposition of triphenylemethyl iodide-$^{13}C_{methyl}$ (**1**) and synthesis of hexaphenylethane-$(^{13}C_{methyl})_2$ (**2**).

We planned to carry out the thermolysis of **1** with $^{13}C_{methyl}$-labeled material. Only if we formed **2** could we expect to observe a dipolar interaction in the NMR spectrum, given its inverse cube dependence on the separating distance of the two magnetic atoms. We have shown previously that the long $^{13}C-^{13}C$ bond lengths extrapolated from dipolar couplings are highly characteristic of hexaarylethanes.[7]

Thermolysis

Calorimetry. Crystals of **1** were analyzed by differential scanning calorimetry. No changes in heat capacity were detected until 85 °C, a temperature much higher than expected due to Gomberg's report of the thermal instability of **1**, at which point several broad endothermic transitions were detected. Following these endotherms, the polyhedral orange crystals had congealed producing a tarlike substance. It is most unlikely that any chemical reaction near this stage would conform to the topochemical principle.

ESR Spectroscopy. A randomly oriented single crystal placed inside a quartz tube was heated in the cavity of an ESR spectrometer. We observed a signal whose intensity increased almost linearly with temperature between room temperature and 70 °C. The growth and dimunition of the ESR signal was fully reversible in this temperature range. Under these conditions only part of the hyperfine field of an isotropic signal was resolved which nevertheless indicates considerable molecular reorientation on the ESR time scale.[8]

Solid-State NMR. The decomposition of a $^{13}C_{methyl}$-enriched sample of **1** was monitored by MAS nuclear magnetic resonance spectroscopy. Enrichment of one site allowed us to follow the chemical history of a single carbon atom as changes occurred in the solid state.

(7) Yannoni, N.; Kahr, B.; Mislow, K. *J. Am. Chem. Soc.* **1988**, *110*, 6670. Kahr, B.; Van Engen, D.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 8305.

(8) Our signal was identical with that from the triphenylmethyl radical of Janzen, obtained by γ-irradiation of crystalline triphenylmethyl carboxylates. Janzen, E. G.; Buchheit, M. *J. Phys. Chem.* **1972**, *76*, 937.

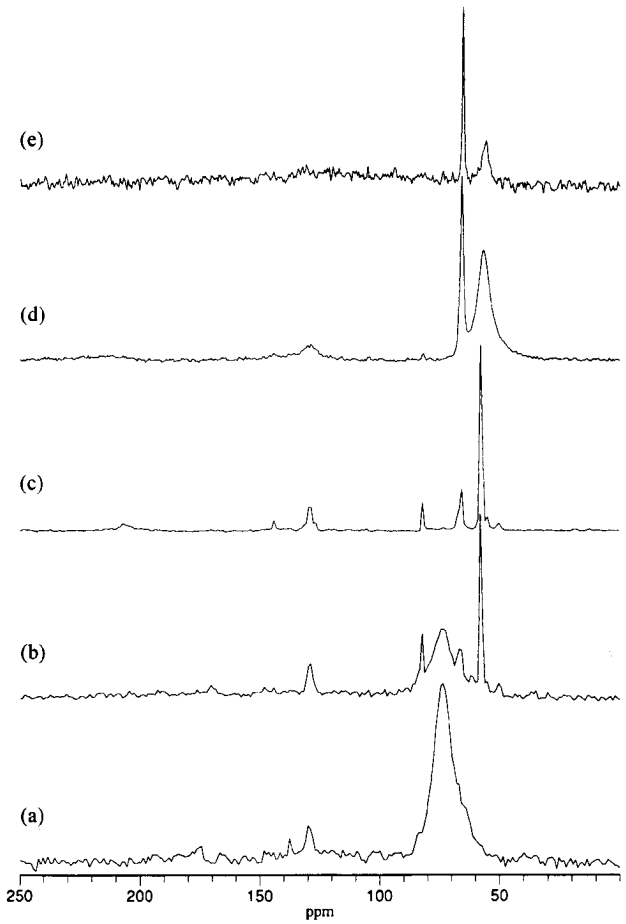


Figure 5. ^{13}C MAS spectra: (a) triphenylmethyl iodide-$^{13}C_{methyl}$ (**1**) at room temperature; (b) after 30 min at 100 °C; (c) after 2 h at 100 °C; (d) after 2 h at 100 °C and then cooled to room temperature; (e) *p*-benzhydryltetraphenylmethane-($^{13}C_{methyl}$)$_2$ (**4**) at room temperature.

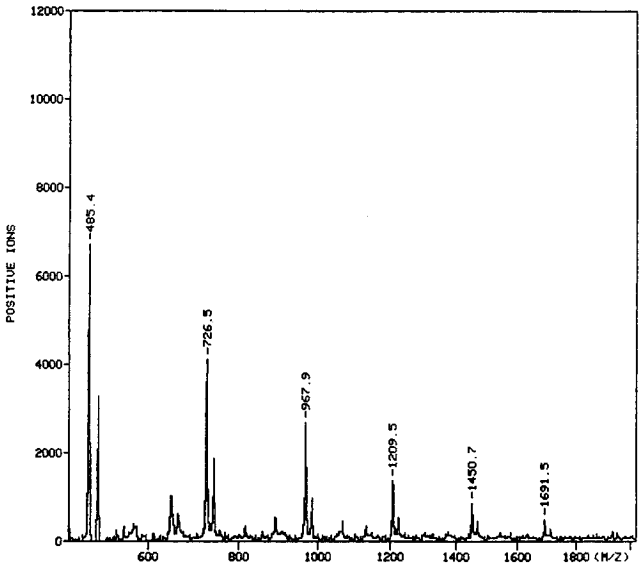


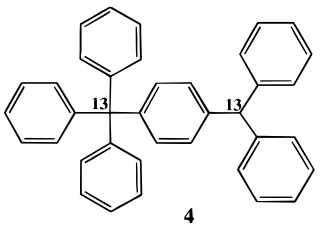
Figure 6. Plasma desorption mass spectrum of decomposed triphenylmethyl iodide-$^{13}C_{methyl}$ (**1**), indicating oligomers of triphenylmethyl-$^{13}C_{methyl}$ and phenylfluorenyl-$^{13}C_{methyl}$ groups.

Large crystals (1 mm^3) of **1** were crushed into a zirconia rotor in preparation for NMR spectroscopy. The room-temperature spectrum of the starting material, **1**-$^{13}C_{methyl}$, consists of a broad (950 Hz, full width at half-maximum) peak (Figure 5a). The line shape is characteristic of a spin-$^1/_2$ nucleus coupled to a quadrupolar nucleus (^{127}I, $S = {}^5/_2$). Ideally, the carbon resonance line should be split into six lines of equal intensity, but when the ^{127}I relaxation rate approaches J_{CI} the multiplet collapses into a single broad band.[9]

Only when the temperature was raised to 100 °C did we begin to observe changes in the NMR spectrum, a finding consistent with the calorimetric results (Figure 5b). A new peak appeared at 57.9 ppm which we recognized as triphenylmethane (**3**) forming at the expense of **1**. We observed a smaller peak at 82.2 ppm for triphenylmethanol, a consequence of reaction with moisture in the air due to the fact that the capped NMR rotors are not completely anaerobic. After heating for 2 h at 100 °C the broad peak was replaced with a sharp peak at 65.7 ppm (Figure 5c). Also evident was a signal at 209.4 ppm characteristic of the triphenylmethyl cation. Lowering the temperature produced dramatic changes in line shapes (Figure 5d). Moreover, a static NMR spectrum showed no evidence of the ~1 kHz dipolar coupling expected for **2**. Interestingly, we find no evidence for the formation of the solution dimer of triphenylmethyl which would be identified by a chemical shift of 137.1 ppm.[10]

The decomposed solid was then dissolved in benzene-d_6 and warmed while oxygen was bubbled through the solution. The ^{13}C NMR spectrum which showed 2 peaks in the solid-state spectrum actually revealed a cluster of peaks at 55 ppm including the major product **3** as well as a cluster of peaks around 66 ppm. These latter peaks, persistent in solution, are unlikely to be associated with **2**.

p-Benzhydryltetraphenylmethane-($^{13}C_{methyl}$)$_2$ (**4**) was synthesized by heating triphenylmethanol-$^{13}C_{methyl}$ in acid in the presence of Zn and $SnCl_2$.[11] The ^{13}C NMR



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solution spectrum of the resultant hydrocarbon gave two principal signals due to the nonequivalent labeled carbon atoms at 65.2 ppm (quaternary) and 56.9 ppm (tertiary, J_{CH} = 129 Hz). The tetraphenylmethyl and triphenylmethane carbons serve as reasonable models for the chemical shifts in the decomposed product. The solid-state NMR spectrum (Figure 5e) showed a sharp peak at 66.1 and a broad peak at 56.2.

Previously, we suggested that the similarity of spectra (e) and (d) was strong evidence for **4** as a major product of the decomposition of **1**.[12] However, we could not chromatographically isolate nor detect **4** in tens of grams of decomposed mixtures. We now must conclude the **4** is not formed in the thermal decomposition of **1**. Moreover, we did not detect 9-phenylfluorene.[13]

Chemical Analysis. The major product from the decomposition of **1** is **3**. A 3.1 g sample of **1** was sealed

(9) Pople, J. A. *Mol. Phys.* **1958**, *1*, 168.
(10) Staab, H. A.; Brettschneider, H.; Brunner, H. *Chem. Ber.* **1970**, *103*, 1101.
(11) Ullman, F.; Borsum, W. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 2877.
(12) Kahr, B. Dissertation, Princeton University, 1988.
(13) A similar result was obtained in the pyrolysis of triphenylmethyl acetate. See: Hurd, C. D.; Mold, J. D. *J. Org. Chem.* **1948**, *13*, 339.

in an H-tube. The side containing the sample was placed in an oil bath, and the empty side was cooled in an acetone bath containing dry ice. After 8 h at 100 °C 2.3 g was collected in the trap which consisted of black crystals of I_2 and colorless crystals of **3**. More than one molecule is reduced for each that is left behind in an oxidized state. Therefore, triphenylmethyl radicals must lose more than one hydrogen atom, presumably in the course of fluorene condensations.[14]

Mass Spectrometry. Electron impact mass spectra (70 keV) of the reaction mixtures were dominated by fragments corresponding to triphenylmethyl and phenylfluorenyl cations. Analysis of the residual material that produced spectrum 5d, by ^{252}Cf plasma desorption mass spectrometry, indicated oligomers with triphenylmethyl and phenylfluorenyl fragments. For example, the peak at *m/z* 1692 (from the labeled sample) would be composed of seven covalently linked triphenylmethyl groups containing five additional degrees of dehydrogenation and terminated by a teriary hydrogen (Figure 6).

Discussion and Conclusion

Despite fearsome comments in the literature, crystalline triphenylmethyl iodide (**1**) is easily handled in the absence of moisture and air. In fact, solid-state NMR experiments indicate that it is difficult to decompose; the bulk is stable up to about 100 °C. This resistance, of course, doomed the proposed synthesis of hexaphenylethane, a molecule whose labile central bond would not withstand the excessive thermal energy. Nevertheless, we believe that the proposed synthetic strategy is sound, and we continue to search for crystalline triphenylmethyl derivatives in which the molecules assemble with the requisite pairwise interdigitation of triphenylmethyl groups. Future work will focus on identifying photolabile[15] precursors which would allow control over the reaction temperature.

Experimental Section

Syntheses. *Triphenylmethyl iodide-$^{13}C_{methyl}$* was prepared from triphenylmethanol-$^{13}C_{methyl}$ and hydrogen iodide according to the procedure of Harmon and Cummings.[2] The crude product was recrystallized from carbon disulfide and petroleum ether as specified by Gomberg,[1] mp 132−133 °C (lit. mp 132 °C). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 67.53 (Ph_3**C**I), δ 127.72, δ 128.54, δ 131.96 (C_{ortho}, C_{meta}, C_{para}), δ 148.08 (d, C_{ipso}, J_{C-C} 47.52 Hz).

p-Benzhydryltetraphenylmethane-($^{13}C_{methyl}$)$_2$ was prepared according to the original procedure of Ullman and Borsum[11] by heating triphenylmethanol-$^{13}C_{methyl}$, zinc, and stannous chloride in an acetic acid/HCl solution. Upon cooling a colorless solid precipitated; mp 224.5−226 °C (lit. mp 225 °C). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 56.87 (Ph_3**C**), J_{C-H} 124.91 Hz, δ 65.23 (Ph_4**C**).

Differential scanning calorimetry was performed with a Perkin-Elmer DSC-7 using indium and mercury standards and liquid nitrogen as a coolant. *ESR Spectroscopy* was performed on a Varian E-line Century Series spectrometer. *Solid-state NMR spectroscopy* was performed on a GE Omega PSG 400WB NMR spectrometer using a Doty Scientific 5 mm high-speed MAS probe in a 9.4 T magnet (proton, 400 MHz). The single-pulse experiment was performed with the decoupler on during acquisition, a P90 of 5 μs and a pulse delay of 10 s. The spinning rate was 4.2 kHz. Solution NMR spectroscopy was performed on a Varian Gemini 200 MHz spectrometer.

Mass Spectrometry. The molecular weights of the nonsublimable material were determined using a Bioion 20R plasma desorption mass spectrometer. This instrument utilizes a ^{252}Cf ionizing source which produces MeV fission fragments. The interaction of the fission fragments with the sample produces ions which are mass analyzed with a time-of-flight spectrometer.[16] The sample (1 μL) dissolved in benzene was applied to a nitrocellulose-coated Mylar target and allowed to dry before inserting it in the spectrometer. The accelerating potential was set at 17 keV. Data were collected for 30 min.

X-ray Crystallography. X-ray intensity measurements were recorded on a Nicolet R3m diffractometer equipped with a nitrogen-flow cooling device. The data were processed with the SHELXTL software. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where w is the weight of a given observation ($w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$).

Single crystals of $C_{19}H_{15}I$ were grown from CS_2 according to the original method of Gomberg.[1] A well-formed polyhedron measuring 0.32 × 0.36 × 0.42 mm was coated with a thin layer of epoxy, mounted on a glass fiber, and centered on the diffractometer. Cell constants and their esd's were determined by a least-squares fit of 25 diffractometer-measured reflections with 45° ≤ 2θ ≤ 50°. The material belongs to the monoclinic crystal system with a = 15.919 (6) Å, b = 10.828 (6) Å, c = 19.397 (11) Å, β = 114.86 °. A density of 1.62 g cm^{-3} was calculated for Z = 8, M = 372.4 g mol^{-1}, μ = 21.3 cm^{-1}, and a volume of 3043 (3) Å^3.

All intensities were measured at 218 ± 3 K with graphite-monochromated Mo Kα (λ = 0.710 69 Å) and an ω-scan technique with a variable scan rate. Background counts were taken for half the scan time at each extreme of the 1.0° scan range. All data (2916) having $k, l \geq 0$ with 3° ≤ 2θ ≤ 50° were measured in this manner.

Crystal decomposition was monitored throughout data collection by remeasuring two standard reflections after every 50 data measurements; no significant variations were recorded. The intensities were reduced by applying Lorentz and polarization corrections. Empirical absorption corrections were applied based on azimuthal scans of 14 suitable reflections; the maximum and minimum transmissions were 0.411 and 0.380, respectively. Equivalent reflections were averaged to give 2676 unique data of which 2334 with $|F_o| > 3\sigma(F_o)$ were considered observed.

An iodine atom was located with the Patterson map in the space group *C*2. Its centrosymmetrically related atom appeared in the first Fourier difference map. Refinement was continued in *C*2/c. All carbon atom positions and phenyl hydrogens were located. All non-hydrogen atoms were refined with anisotropic thermal parameters. Phenyl hydrogen atoms were included at idealized positions (C−H = 0.96 Å, C−C−H = 120.0°) and varied with a riding model. Refinement converged (shift/error ≤ 0.1), R = 0.038, R_w = 0.033 for 181 parameters. A final difference map was featureless with a maximum peak 0.86 e Å^{-3} near I(1).

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Supporting Information Available: Bond lengths, valence angles, and positional parameters (3 pages); table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(14) Lewis, H. G.; Owen, E. D. *J. Chem. Soc. B* **1967**, 422.

(15) We failed to photolytically decompose **1**. A 200 W incandescent white light shined directly on orange crystals of **1** did not produce the liberation of iodine as evidenced by darkening. Presumably, I_2 pushes the photostationary state in the reverse direction, back toward the formation of **1**.

(16) Wood, K. V.; Bonham, C.; Hipskind, J.; Nicholson, R. L. *Phytochemistry* **1994**, *37*, 557.